

Date of Deposit December 22, 2003

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TITLE OF THE INVENTION

COLD STORAGE AGENT, COLD INSULATING MATERIAL, AND FREEZER

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BACKGROUND OF THE INVENTION

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5 Field of the Invention

The present invention relates to a cold storage agent, a cold insulating material, and a freezer. In the present invention, the cold insulating material means a material obtained by dissolving the cold storage agent according to the present invention in water, and freezing the aqueous solution of the cold storage agent in a container. The freezer according to the present invention includes a freezing case and a transport container.

Description of Prior Art

15 As for a freezing mixture, a combination of NH_4Cl and KNO_3 , a combination of NaNO_3 and NH_4NO_3 , or a combination of KNO_3 and NH_4SCN is known. However, a cold storage agent which can be used as a substitute for dry ice, that is, a cold storage agent which can provide
20 temperatures optimum for freezing (-35 to -50°C) has not yet been found.

SUMMARY OF THE INVENTION

25 The present invention provides a cold storage agent comprised of a combination of two kinds of salts capable of providing a lower temperature as compared with a cold storage agent comprised of a single salt, and a cold

insulating material obtained by dissolving such a cold storage agent in water, and freezing the aqueous solution of the cold storage agent in a container made of polyethylene or the like and having a thickness of 1 to 3
5 mm. More specifically, the present invention provides a cold storage agent comprised of a combination of salts capable of obtaining a cold storage effect of maintaining a low temperature of -35°C or lower, and a cold insulating material prepared using such a cold storage agent. Further,
10 the present invention provides a freezer which contains such a cold insulating material capable of providing a low temperature of -35°C or lower, and can maintain the temperature of the inside thereof at -20°C or lower.

The present inventor has prepared an aqueous
15 solution of the cold storage agent comprised of a combination of at least two salts composed of identical negative ions and different positive ions. An example of a negative ion includes chloride ion, sulfate ion, or nitrate ion. The salt may be a monovalent salt or a bivalent salt.
20 In the case of a monovalent salt, an example of a positive ion includes sodium ion, potassium ion, or ammonium ion. In the case of a bivalent salt, an example of a positive ion includes magnesium ion or calcium ion.

In two salts, negative ions should be identical,
25 and a combination of positive ions should be a combination of monovalent ion and monovalent ion, or a combination of bivalent ion and bivalent ion. That is, the cold storage

agent of the present invention is comprised of a combination of a salt composed of a monovalent negative ion and a monovalent positive ion and a salt composed of a monovalent negative ion and a monovalent positive ion. A
5 combination of a salt composed of a monovalent negative ion and a monovalent positive ion and a salt composed of a monovalent negative ion and a bivalent positive ion should be excluded.

As described above, in the present invention, an
10 example of a negative ion includes chloride ion, sulfate ion, or nitrate ion. Among them, chloride ion (Cl^-) is preferable because it has been confirmed from experimental results that chloride ion has the effect of markedly lowering melting point and prolonging cold storage duration.
15 As for a positive ion, in the case of a monovalent salt, sodium ion (Na^+), potassium ion (K^+), or ammonium ion (NH_4^+) can be mentioned. In the case of a bivalent salt, magnesium ion (Mg^{2+}) or calcium ion (Ca^{2+}) is preferable.

Accordingly, in the present invention, a preferred
20 example of a combination of monovalent salts includes a combination of NaCl and KCl , a combination of NaCl and NH_4Cl , a combination of KCl and NH_4Cl , or a combination of NaCl , KCl and NH_4Cl . As for a combination of bivalent salts as chloride, a combination of MgCl_2 and CaCl_2 can be
25 mentioned.

Among bivalent salts, a combination of a bivalent salt composed of chloride ion as a negative ion and calcium

ion as a positive ion and a bivalent salt composed of chloride ion as a negative ion and magnesium ion as a positive ion is preferable in terms of lowering of melting point and prolongation of cold storage duration as compared
5 with a single chloride salt. Further, such combined bivalent salts can provide a low temperature of -37°C (in the case of a combination of magnesium chloride as a main component and calcium chloride) or -45°C (in the case of a combination of calcium chloride as a main component and
10 magnesium chloride), and therefore a cold storage agent comprised of such combined bivalent salts can be used as a substitute for dry ice.

Furthermore, a freezer or a transport container capable of maintaining the temperature of the inside
15 thereof at a low temperature of -20°C or lower for a long period of time can be achieved by setting a cold insulating material obtained by freezing such a cold storage agent of the present invention in an accommodation member, in the inside of the freezer. Since such a cold insulating
20 material can maintain the temperature of the inside of the freezer at -20°C or lower for a long period of time, it can be suitably used for freezing food, as a substitute for dry ice. The cold insulating material is preferably set in the upper portion of the freezer, but it is not always
25 necessary to set the cold insulating material in the upper portion of the freezer as long as air in the freezer is stirred by using a fan.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph which provides a comparison of a change in surface temperature between a cold insulating material according to the present invention and a conventional cold insulating material; and

FIG. 2 is a schematic illustration which shows the inside of a freezer containing the cold insulating material according to the present invention.

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DETAILED DESCRIPTION OF THE INVENTION

Hereinbelow, a description will be made with regard to embodiments of the present invention.

1/2 to 1/10, preferably, 1/3 to 1/5 wt% of ammonium chloride (NH_4Cl) is added with respect to 1 wt% of sodium chloride (NaCl) or potassium chloride (KCl). Alternatively, 1/3 to 1/5 wt% of sodium chloride (NaCl) or potassium chloride (KCl) may be added with respect to 1 wt% of ammonium chloride (NH_4Cl).

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The basic concept regarding the above case is as follows. 1/3 to 1/5 wt% of a main component is reduced from an optimum amount (wt%) of the main component when used singly, and the reduced amount (1/3 to 1/5 wt%) of the main component is added to another salt. In this case, the total amount of the main component is substantially the same as the optimum amount (wt%). Alternatively, 1/3 to 1/5 wt% of the optimum amount of the main component when used singly may be added to another salt.

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It is also possible to obtain a preferable result by reducing 1/3 to 1/5 wt% of the main component (sodium chloride (NaCl) or potassium chloride (KCl)), and adding ammonium chloride (NH₄Cl) as much as the above reduced amount so that the total amount of the respective components becomes substantially the same as the amount of the main component before reduction. The same thing can be said for the case of a combination of bivalent salts (magnesium chloride (MgCl₂) and calcium chloride (CaCl₂)).

For example, 1/2 to 1/8 wt% of calcium chloride (CaCl₂) is added with respect to 1 wt% of magnesium chloride (MgCl₂). Alternatively, 2 to 8 wt% of calcium chloride (CaCl₂) may be added with respect to 20 wt% of magnesium chloride (MgCl₂) that is an optimum amount of magnesium chloride when used singly. It is preferred that the weight percentage of the main component is in the range of 10 to 25. The thus obtained cold storage agent is dissolved in water to prepare an aqueous solution thereof, and the prepared aqueous solution is placed in a container made of polyethylene or the like and then frozen, to obtain a cold insulating material.

In the present invention, the cold insulating material obtained by dissolving a mixture of magnesium chloride (MgCl₂) as a main component and calcium chloride (CaCl₂) in water and freezing the aqueous solution of the mixture can maintain a low temperature of -36°C and has a longer cold storage duration as compared with a cold

insulating material comprised of magnesium chloride (MgCl_2) alone. On the other hand, the cold insulating material comprised of a mixture of calcium chloride (CaCl_2) as a main component and magnesium chloride (MgCl_2) can provide a lower temperature of -45°C . Therefore, such a cold insulating material obtained by freezing the cold storage agent of the present invention in a container can be used as a substitute for dry ice. Further, the cold insulating material obtained by dissolving a mixture of sodium chloride (NaCl) as a main component (having a melting point of -20°C when used singly) and ammonium chloride (NH_4Cl) in water, and freezing the aqueous solution of the mixture has a lower melting point of -25°C and a long cold storage duration (see FIG. 1). As described above, such a mixed cold storage agent (cold insulating material) has an excellent cold storage effect as compared with a cold storage agent (cold insulating material) comprised of a single component.

FIG. 2 is a schematic illustration which shows the inside of the freezer containing the cold insulating material according to the present invention. As shown in FIG. 2, a cold insulating material 12 obtained by freezing the cold storage agent dissolved in water contained in an accommodation member is placed inside a freezer 10. A transport container is also included in such a freezer. The cold insulating material is placed in the upper portion of the freezer, and therefore, a storage part 14 for

setting the cold insulating material is provided in the upper portion of the freezer. The freezer may have a fan 16 for uniformly filling the inside of the freezer with cold air generated by the cold insulating material placed in the storage part 14, and further a cold air blowing means 18 for blowing cold air generated by the cold insulating material placed in the upper portion of the freezer in the downward direction.

Example 1

Each of a 23 wt% aqueous sodium chloride solution and an aqueous solution containing 17 wt% of sodium chloride and 5 wt% of ammonium chloride was placed in a container made of polyethylene and having a thickness of 1 mm, and then frozen. Thereafter, the melting point of each of the frozen aqueous solutions was measured, and the former was -20°C and the latter was -25°C. These frozen aqueous solutions had the same cold storage duration.

Example 2

Each of a 20 wt% aqueous potassium chloride solution and an aqueous solution containing 15 wt% of potassium chloride and 5 wt% of ammonium chloride was placed in a container made of polyethylene and having a thickness of 1 mm, and then frozen. Thereafter, the melting point of each of the frozen aqueous solutions was measured, and the former was -10.5°C and the latter was -17°C. These frozen aqueous solutions had the same cold storage duration.

Example 3

Each of a 20 wt% aqueous ammonium chloride solution and an aqueous solution containing 20 wt% of ammonium chloride and 5 wt% of potassium chloride was placed in a container made of polyethylene and having a thickness of 1 mm, and then frozen. Thereafter, the melting point of each of the frozen aqueous solutions was measured, and the former was -16°C and the latter was -17.5°C . The cold storage duration of the latter was 1.15 times longer than that of the former.

Example 4

Table 1

	minutes						
	60	120	180	260	300	360	420
MgCl ₂ 15%	-81	-31	-31	-29	-23	-15	-12
MgCl ₂ 15 + CaCl ₂ 5%	-42	-40	-36	-33	-26	-16	-5
MgCl ₂ 15 + CaCl ₂ 2.5%	-42	-34	-32	-30	-24	-15	-12
MgCl ₂ 20 + CaCl ₂ 7.5%	-45	-37	-34	-29	-18	-8	-3
MgCl ₂ 20 + CaCl ₂ 2.5%	-35	-34	-33	-30	-20	-7	-3

A 15 wt% aqueous magnesium chloride solution, an aqueous solution containing 15 wt% of magnesium chloride and 2.5 wt% of calcium chloride, an aqueous solution containing 15 wt% of magnesium chloride and 5 wt% of calcium chloride, an aqueous solution containing 20 wt% of magnesium chloride and 7.5 wt% of calcium chloride, and an aqueous solution containing 20 wt% of magnesium chloride and 2.5 wt% of calcium chloride were prepared as cold storage agents. Each of the cold storage agents was placed

in a container made of polyethylene and having a thickness of 1 mm and a capacity of 550 mL, and was then frozen. The thus obtained each of the cold insulating materials was placed in a styrofoam box having a size of 30 × 21 × 12 cm and a thickness of 2 cm, and a change in surface temperature of cold insulating material was measured. The melting point of each of the cold insulating materials is shown in Table 1.

The cold insulating material comprised of 15 wt% of magnesium chloride alone had a melting point of -31°C. On the other hand, in the case of the cold insulating material comprised of a mixture of magnesium chloride and calcium chloride, the cold insulating material containing 2.5 wt% of calcium chloride had a lower melting point as compared with the cold insulating material comprised of magnesium chloride alone, and the cold insulating material containing 5 wt% or more of calcium chloride had a markedly lowered melting point. Further, the cold insulating material containing 20 wt% of magnesium chloride had a still lower melting point.

Moreover, (a) a cold insulating material containing 15 wt% of magnesium chloride and 5 wt% of calcium chloride, (b) a cold insulating material containing 15 wt% of magnesium chloride alone, (c) a cold insulating material containing 17 wt% of sodium chloride and 5 wt% of ammonium chloride, and (d) a cold insulating material containing 23 wt% of sodium chloride alone were prepared.

For each of the cold insulating materials, a change in surface temperature of cold insulating material when two blocks of the cold insulating material were placed in a freezer was measured. The result is shown in FIG. 1, wherein ▲-▲ represents the cold insulating material (a), ◆-◆ represents the cold insulating material (b), Δ-Δ represents the cold insulating material (c), and ◇-◇ represents the cold insulating material (d). As shown in FIG. 1, the cold insulating material comprised of a mixture of chloride salts showed a lower temperature as compared with the cold insulating material comprised of a single chloride salt, and there was no difference in change in surface temperature with the passage of time between them. Specifically, the cold insulating material comprised of a mixture of magnesium chloride and calcium chloride (a) showed a lower temperature as compared with the cold insulating material comprised of magnesium chloride alone (b). Similarly, the cold insulating material comprised of a mixture of sodium chloride and ammonium chloride (c) showed a lower temperature as compared with the cold insulating material comprised of sodium chloride alone (d). In addition, there was no difference in change in surface temperature with the passage of time between them.

Example 5

A cold insulating material comprised of 10 wt% of potassium chloride alone had a melting point of -11°C . On the other hand, a cold insulating material comprised of a

mixture of 10 wt% of potassium chloride and 3 wt% of ammonium chloride had a melting point of -13°C .

Example 6

5 A cold insulating material comprised of 15 to 17 wt% of calcium chloride alone had a melting point of -44°C . On the other hand, a cold insulating material comprised of a mixture of 15 wt% of calcium chloride and 5 wt% of magnesium chloride had a melting point of -47.5°C .